

reparation of Sodium Perborate by Electrochemical Method

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The anodic electro-synthesis of sodium perborate at a smooth platinum anode was studied by varying anode current density, temperature and addition agents and their composition. The optimum parameters for electrolysis are reported. The crystallization and stabilization of perborate crystals were also studied.

Key words: Sodium perborate, platinum anode, addition agents

Introduction

Sodium perborate finds extensive use in household laundry, dry-bleach and detergent formulations. It is also used in hard-surface cleansers, denture cleansers, cosmetics, vat and sulphur dye oxidation and textile bleaching.

Though the chemical method of preparation is preferred by the industry [1], interest is also shown in the electrochemical process, especially for small tonnage plants [2].

Many references are available in the literature for the preparation of sodium perborate by an electrolytic process [3]. They mainly deal with the influence of anode and cathode materials [4-7], composition of the electrolyte [9-10], different addition agents [6,8,11] and operating current density [12].

In our earlier communication [13], studies on the effect of anode current density, temperature and concentration of borax and sodium carbonate on the current efficiency were reported. In this paper the effect of cathode current density, addition agents and the presence or absence of diaphragm are reported.

Experimental

Cell assembly

A jacketed glass container of 280 ml capacity fitted with a PVC cover having slots to introduce the smooth platinum anode (4.2 cm x 2.2 cm x 0.1 mm) flanked by two perforated stainless steel cathodes (7.1

cm x 6.1 cm) at an interelectrode distance of 0.5 cm and a sample inlet acted as the cell assembly. Cold water brine was circulated through the outer jacket of the cell to maintain the desired temperature. The solution was mechanically stirred with a glass stirrer to keep the temperature of the electrolyte uniform. (sodium carbonate - borax - sodium bicarbonate). When the cathodes were wound with asbestos rope, it served as a diaphragm.

Electrolysis procedure

The electrolysis was started after the desired temperature had reached in the cell. Samples were taken periodically and analysed with permanganate titration to calculate the current efficiency [4]. To maintain a constant volume in the cell, electrolyte was replenished with the original solution after removal of each sample.

At the end of electrolysis, the solution was cooled further to a temperature of 275 - 276 K to make the perborate to crystallize. Decantation, filtration, washing and drying isolated the crystals of sodium perborate.

Results and discussion

Effect of duration of electrolysis on current efficiency

Fig. 1 gives the results of one experiment where the current efficiency for perborate formation was followed with the duration of electrolysis. It is seen that the current efficiency decreased with the duration. This may be due to the self-decomposition of perborate with in

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concentration. Through perborate is known to have a solubility of about 5 g/l in a normal solution of carbonate and bicarbonate at 284 K [1], it easily forms a supersaturated solution when a concentration of 20 g/l is reached. The presence of excess of solid perborate or carbonate and borax (by addition of excess of these substances) did not prevent the formation of the supersaturated solution until a temperature of 275 K is reached by further cooling of the solution.

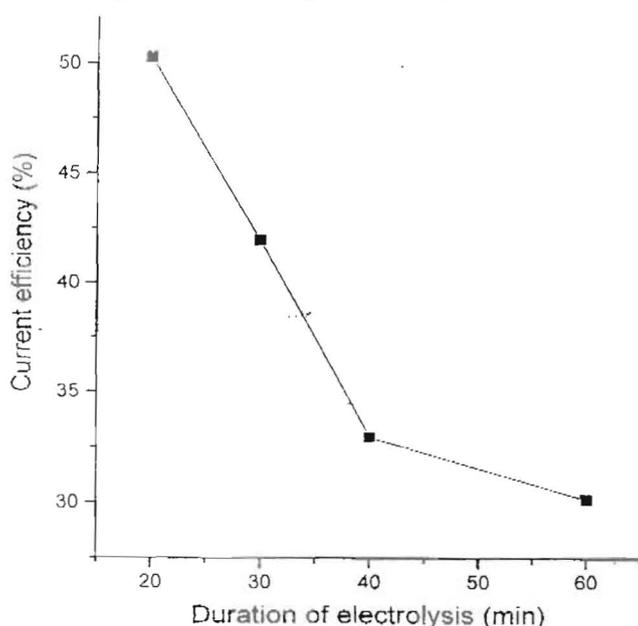


Fig. 1. Sodium perborate electrosynthesis. Conditions as given in Table 2 (without replenishment of electrolyte)

Effect of anode current density

Table 1 gives the effect of anode current density on current efficiency. It is seen that at first, the efficiency increased as the current density is raised from 20 to 40 A/dm² and later on, it decreased with further increase in current density to 60 and 80 A/dm². This may be attributed to the evolution of oxygen at higher current densities. Hence the optimum current density seems to be 40 A/dm². This is in confirmation with the reported works of Wiel et al. [16], where the current efficiency was shown to decrease after 40 A/dm². Matsuda has reported that the current efficiency at first increased with current density and reached a plateau at 40 A/dm² [17]. However, a higher efficiency of about 69% has been claimed even at higher current densities, viz. 80 A/dm² by Mollard Paul [15]

Table 1. Effect of anode current density on current efficiency
Electrolyte: Borax (40 g/l) + sodium carbonate (130 g/l) + sodium bicarbonate (20 g/l) + urea (0.2 g/l) + magnesium nitrate (0.2 g/l) Temperature: 283 K

Duration (min)	Anode current density (A/dm ²)	Current passed (A)	Voltage (V)	Concn. of perborate (g/l)	Current efficiency (%)	Energy consumption (KWh/kg)
120	20	1.75	3.05	13.60	38.00	2.80
60	40	3.50	5.30	16.64	47.60	4.00
40	60	5.25	6.00	14.60	40.80	5.10
30	80	7.00	6.50	15.00	41.80	5.40

Table 2. Effect of addition agents on the current efficiency
Electrolyte: Borax (40 g/l) + sodium carbonate (130 g/l) + sodium bicarbonate (20 g/l) and addition agent Temperature: 283 K Current density: 40 A/dm²

S. No	Addition agent	Concentration (g/l)	Concentration of perborate (g/l)	Current efficiency (%)
1	Magnesium silicate	1.0	18.4	
2	Magnesium nitrate + urea	0.2	17.0	51.2
				47.2
3	Magnesium silicate + urea + magnesium nitrate	1.0	16.6	
		0.2		46.6
4	Magnesium silicate + Glycerol	1.0	15.6	
				43.4
5	Magnesium silicate	2.0	15.6	
6	Sodium orthophosphate	14.0	14.5	43.4
				40.3
7	Magnesium silicate + sodium nitrate	1.0	12.7	
		0.2		35.9
8	Magnesium nitrate + urea + thiourea	0.2	8.8	
		2.0		24.5

Effect of addition agents

Perborate is decomposed easily, especially in an alkaline solution by the presence of metallic impurities such as iron (which is invariably present in commercial sodium carbonate) and lead. Hence, addition agents are needed to stabilize the perborate. Table 2 shows the effect of different addition agents on current efficiency. Of these, magnesium silicate at 1 g/l is seen to give the highest efficiency. Magnesium nitrate and urea each at 0.2 g/l are claimed not only to give good

current efficiency but also reduce the platinum consumption [11]. Different samples of the solution obtained by electrolysis were treated with the following four addition agents each at 2 g/l (i) thiourea, (ii) sulphosalicylic acid (iii) succinic acid and (iv) sodium orthophosphate. Of these, thiourea showed good stabilizing effect followed by sulphosalicylic acid on testing the solution after four days. The latter two compounds did not show a stabilising influence.

Electrolyte replenishment

Table 3 shows the effect of continuous removal of electrolyte and addition of make-up electrolyte. The make-up electrolyte contained in addition to borax, sodium hydroxide for converting the bicarbonate formed during electrolysis into carbonate. It is seen that current efficiencies are slightly lower with the replenishment. This may be due to the decomposition of perborate by the higher alkalinity caused. When the make-up solution containing only the borax or the original electrolyte solution was used, the current efficiency did not show any change.

Table 3. Effect of replenishment of electrolyte. Solution used for replenishment: borax (50 g/l) + sodium hydroxide (10 g/l) Anode current density: 80 A/dm²

Duration of electrolysis (min)	Quantity of electricity (A)	Current efficiency	
		without replenishment	with replenishment
20	2.3	50.3	48.3
30	3.5	42.0	40.7
40	4.7	33.0	34.7
60	7.0	30.2	27.5

Effect of the presence or absence of a diaphragm and stirring the electrolyte

The absence of a diaphragm did not result in any decrease of the current efficiency. The effect of stirring was to provide uniform temperature conditions in the cell which resulted in better current efficiency, though the voltage was higher in the absence of stirring. The decreased temperature between the electrodes due to stirring evidently causes the latter effect.

Experiments on crystallization of perborate

Since perborate easily forms a supersaturated solution, which resulted in decreased current efficiency, attempts were made to crystallize the perborate as and when it was formed. For this, the following experiments were carried out.

- (i). Solid perborate was used for preparing a saturated solution of perborate with the usual borax-carbonate electrolyte used in these experiments and this electrolyte was used for electrolysis.
- (ii). To a 10 - 12 g/l perborate solution formed during electrolysis, perborate seeds were added to give a final concentration of 20 g/l.
- (iii). A saturated solution of carbonate and borax was used.
- (iv). The electrolyte was circulated continuously through a cell crystalliser arrangement, where the crystalliser was maintained at a temperature of 5 K lower than the cell temperature.

In all these experiments, in spite of the presence of excess borax and sodium carbonate/solid perborate or the addition of solid seeds of perborate, the concentration of perborate continued to rise beyond its saturation limit.

Conclusion

An anode current density of 20 A/dm² and a stabilizer (magnesium silicate) concentration of 1 g/l were found to be optimum for the electrolysis. Continuous replenishment of electrolyte with borax and sodium hydroxide slightly decreased the current efficiency, whereas addition of borax and carbonate during electrolysis did not have much influence on the current efficiency.

It was not possible to prevent the supersaturating of perborate by the addition of solid perborate as seed or by use a saturated electrolyte of borax and carbonate/sodium perborate. The solid perborate in spite of the addition of stabilizers was found to be unstable.

Further experiments on crystallization and stabilisation of perborate are in progress.

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